

# The Photochemistry of Propane at High Photon Energies (8.4-21.2 eV)\*

R. E. Rebbert, S. G. Lias, and P. Ausloos

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

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Neon and helium resonance lamps, which deliver photons of 16.7–16.8 eV and 21.2 eV energy, respectively, have been used to photolyze  $C_3H_8$ ,  $C_3D_8$ ,  $C_3H_8$ - $C_3D_8$  (1:1) mixtures, and  $CD_3CH_2CD_3$  and the results obtained at the two energies are compared. In particular, it is noted that although the quantum yield of ionization in propane is unity at 16.7–16.8 eV, when the energy is raised still further to 21.2 eV, the probability of ionization apparently diminishes to 0.93, an observation which suggests that at 21.2 eV, superexcited states may be reached whose dissociation into neutral fragments competes with ionization.

The quantum yields of the lower hydrocarbon products formed in the presence of a radical scavenger in  $C_3H_8$  and  $C_3D_8$  are reported, and are compared with quantum yields of products formed in the vacuum ultraviolet photolysis at lower energies. (Quantum yields of products formed at 8.4 eV and 10.0 eV are reported here for the first time.) Acetylene is formed as a product in the decomposition of the neutral excited propane molecule, and its yield increases in importance with increasing energy; at 16.7–16.8 eV, where all product formation can be traced to ionic processes, acetylene is formed in negligible yields. It is concluded that ionic processes in propane do not lead to the formation of acetylene, and the observation of this product in radiolytic systems may be a reliable indicator of the relative importance of neutral excited molecule decomposition processes.

From the results obtained with the  $C_3H_8$ - $C_3D_8$  (1:1) mixture, and with  $CD_3CH_2CD_3$ , details of the ion-molecule reaction mechanisms and the unimolecular decomposition of the propane ion are derived.

**Key words:** Ion-molecule reaction; photoionization; propane; quantum yields; rare-gas resonance radiation; unimolecular dissociation.

## 1. Introduction

In the past, most photolysis studies in the vacuum ultraviolet region have been carried out at energies below 11.8 eV (104.8 nm). The lamps commonly used in this energy region are rare gas resonance lamps, which deliver the resonance lines of xenon (8.4 eV, 147.0 nm), krypton (10.0 eV, 123.6 nm), or argon (11.6–11.8 eV, 106.7–104.8 nm). Higher energy resonance lamps could not be made because of the lack of suitable windows which would transmit photons above 11.8 eV in energy. Recently, in this laboratory, enclosed neon and helium lamps have been fabricated; their operational characteristics have been described in detail [1].<sup>1</sup> These lamps, which deliver the neon and helium resonance lines (16.7–16.8 eV and 21.2 eV, respectively), are fitted with windows made of thin (2000–4000 Å) films of aluminum.

Photolysis studies in this high energy region are, of course, still very rare. Only a few studies, limited in

scope, of the chemical effects brought about in methane [2–4] and in argon-propane mixtures [5] by helium resonance radiation have been published. One of these studies [2] was carried out with a differentially pumped windowless helium lamp; under such conditions, the investigator is restricted to a low pressure range. No studies at pressures above the millitorr range utilizing neon resonance radiation have so far appeared in the literature.

This paper reports the results of a study where, for the first time, a compound is exposed to both neon and helium resonance radiation, and the chemical effects at the two energies are compared. Propane was chosen as the subject compound because the unimolecular and bimolecular (ionic and free radical) processes occurring in this system have been extensively investigated [6] and are well understood. In the high energy region used in this study, chemical effects will be brought about nearly exclusively through ionic processes. A comparison of the effects brought about by photons of two different energies may highlight subtle differences, and, therefore, increase our understanding

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<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

of the activation processes in the high energy range. These results should also be of value in interpreting results obtained in systems exposed to high energy radiation (x rays, gamma rays, energetic electrons, etc.) where end product formation is brought about not only through ionic processes similar to those observed here, but also through the unimolecular decomposition of superexcited molecules.

## 2. Experimental Procedure

The reaction vessel and the resonance lamps used in this study have been described before [1]. Both the neon and helium resonance lamps were provided with 2000 Å aluminum windows which were entirely leak-free, and could withstand a pressure differential between the reaction vessel and the interior of the resonance lamp of 100 torr or more. At the start of the study the photon flux of the helium and neon resonance lamps was, respectively,  $5 \times 10^{13}$  and  $7 \times 10^{12}$  quanta/s. It was ascertained that the helium and neon lamps were essentially monochromatic throughout the study by introducing neon and helium, respectively, into the first compartment of a double cell arrangement described before [1]. It was ascertained that neon gas placed in the sample cell absorbed the neon resonance radiation and was transparent to the radiation emanating from the helium lamp, while helium was transparent to the photons from the neon lamp and absorbed those from the helium lamp. In the course of an experiment, either at the neon or the helium line, the decay in the light flux was no more than five percent from beginning to end.

The analytical procedures, as well as the purification of the materials used in this study, have been described [7].

In most experiments, quantum yield determinations of the end product were made which were based on saturation ion currents measured periodically during the course of an irradiation [1, 7]. In these experiments, approximately 15 torr of a nonabsorbing inert gas (helium in the neon resonance line experiments, and vice versa) was added; it has been shown that the addition of such an inert will generally improve the definition of the plateau of the saturation ion current [1, 8], and therefore lead to a more accurate determination of the quantum yields of the end products formed in the photolysis.

Allene and methylacetylene were noted as products at 8.4 to 11.8 eV, but their quantum yields were not determined.

## 3. Results and Discussion

### 3.1. Units

In a photolysis experiment carried out at an energy below the ionization energy of the compound of interest, a quantum yield of a given product,  $\Phi$ , is simply the probability that the particular product will result when an excited molecule undergoes unimolecular de-

composition in the system under a particular set of conditions. In photoionization experiments, where some quanta produce ions, it has been found convenient in the past [7] to use two systems of units depending on whether a process involving a neutral excited molecule or an ionic process is being considered. Thus, the yields of products resulting from nonionic processes were expressed in units of  $M(X)/N_{ex}$ , or molecules  $M$  of product  $X$  formed per neutral excited molecule dissociating in the system,  $N_{ex}$ ; for photolysis in the sub-ionization region  $M(X)/N_{ex}$  is simply the quantum yield. Ionic product yields, on the other hand, have generally been expressed in ion pair yield units, that is, as  $M(X)/N_+$ , or molecules  $M$  of product  $X$  formed per positive ion formed in the system,  $N_+$ .

Experimentally, an ion-pair yield is easily measured since  $N_+$  is directly determined by measuring the saturation ion current:

$$N_+ = I \times t(s) \times 6.24 \times 10^{18} \text{ ions/C}$$

(where  $I$  is the saturation ion current in amps and  $C$  is coulombs). If the quantum yield of ionization,  $\Phi_+$ , is known, then  $M(X)/N_{ex}$  can be determined from the relationship:

$$\frac{M(X)}{N_{ex}} = \frac{M(X)}{N_+} \times \Phi_+ \times \frac{1}{1 - \Phi_+} = \Phi \times \frac{1}{1 - \Phi_+}$$

The overall quantum yield is thus:

$$\Phi = \frac{M(X)}{N_{ex} + N_+}$$

In this paper, we are concerned mainly with results obtained at very high energies where all, or almost all, product formation results from ionic processes; under these conditions the quantum yields and ion pair yields are essentially identical. The products formed at these energies are, however, compared with products observed in the photolysis at lower energies. All product yields are expressed in quantum yield units. Thus, in the 8.4 and 10.0 eV experiments, no ionization occurs, and there is no complication about the yield units. At 11.6–11.8 eV, on the other hand, only 73 percent (table 1) of the quanta absorbed lead to neutral excited molecule formation. Therefore, an

TABLE 1. Ionization quantum yields and extinction coefficients of propane<sup>a</sup>

Photon energy	$\epsilon \text{ cm}^{-1} \text{ atm}^{-1}$	$\Phi_+$
11.6–11.8 eV	n.d.	0.27 <sup>b</sup>
16.7–16.8 eV	2950	1.00
21.2 eV	2240	0.93

<sup>a</sup> Argon lamp: 70 percent 11.6 eV, 30 percent 11.8 eV.

<sup>b</sup> C. E. Klotz, to be published.

estimation of the probability that the decomposition of the superexcited propane molecule formed at this energy would lead to the formation of a given product requires that the overall quantum yields be divided by 0.73; the quantum yields can be translated into ion pair yields, if the product of interest is of ionic origin, by dividing by 0.27.

### 3.2. Ionization Quantum Yields

In table 1 are given the extinction coefficients and ionization quantum yields of propane at the argon, neon, and helium resonance lines, 11.6–11.8 eV (106.7–104.8 nm), 16.7–16.8 eV (74.4–73.6 nm) and 21.2 eV (58.4 nm), respectively [8]. It is noteworthy that when the photon energy is increased from 11.6–11.8 eV to 16.6–16.7 eV, the quantum yield of ionization increases from 0.27 to a value of unity, but when the photon energy is further increased to 21.2 eV, the quantum yield of ionization seems to decrease to a value lower than unity. The value reported for 21.2 eV is based on the saturation ion current measurements shown in figure 1. At this wavelength, hydrogen has an ionization quantum yield of unity [8–10]; because at the helium resonance line, hydrogen has a low extinction coefficient [ $\epsilon=185$ ], the saturation current measured in hydrogen has a well defined plateau extending over a range of several hundred volts (fig. 1). Therefore, the hydrogen saturation ion current is an ideal standard against which to compare saturation ion currents measured in other compounds at the same light flux. Under pressure conditions where all incident photons are absorbed, the quantum yield of ionization of the unknown is given simply by the ratio of the two plateau values of the saturation ion current measurements. As the figure clearly shows, the plateau of the saturation ion current measured in propane at this energy is not as well defined as that for hydrogen, but seems to fall below the plateau measured in hydrogen.

A recent study from this laboratory [8] reported that the ionization quantum yields of  $C_1$  to  $C_4$  alkanes at the neon resonance lines (16.7–16.8 eV) are all unity. The apparent drop in the importance of ionization in propane as the energy is raised to 21.2 eV is also observed in these other alkanes [12, 13]. This is an interesting observation which, if correct, suggests that in alkanes which have absorbed a 21.2 eV photon, superexcited states may be reached which dissociate so rapidly that decomposition can compete with ionization. Overall product distributions such as those shown in the table do not, of course, in themselves give us much information about photolytic mechanisms. Additional information, such as that obtained from deuterium labeling experiments is required in order to trace the modes of formation of a given product. Such experiments have demonstrated [17–19] that neutral excited propane molecules undergo the following primary processes:

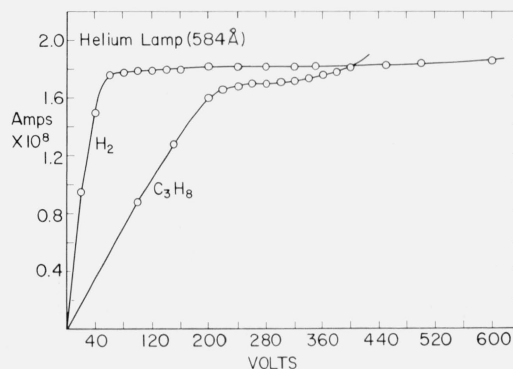
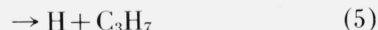
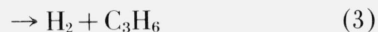
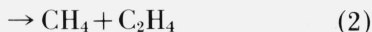
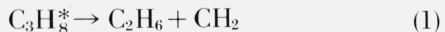


FIGURE 1. Saturation ion currents measured in 5 torr of hydrogen and in 0.2 torr of  $C_3H_8$  in the presence 20 torr of helium, irradiated with the 21.2 eV helium resonance line.

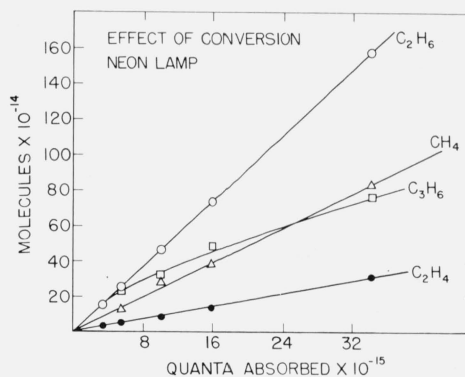


FIGURE 2. Molecules of ethane, methane, propylene, and ethylene formed in the 16.7–16.8 eV photolysis of a propane-oxygen-helium (1.0:0.03:8.3) mixture at a total pressure of 28 torr, as a function of the number of quanta absorbed by the propane.

### 3.3. Photolytic Product Yields

Figure 2 shows the number of molecules of various lower hydrocarbon products formed as a function of the number of 16.7–16.8 eV quanta absorbed in a propane-oxygen-helium (1.0:0.03:8.3) mixture at a propane pressure of 3 torr. The amounts of the methane, ethane, and ethylene products formed increase linearly with the number of photons absorbed. Propylene, on the other hand, does not show such a linear relationship. This behavior may be accounted for by several factors. For instance, it has been shown before [5] that one precursor of propylene in propane is the propyl ion, and this ion may react with accumulated products at high conversions. Another plausible

TABLE 2. Quantum yields of end products in the photolysis of  $C_3H_8$ 

Photon energy	Propane	Scavenger	Methane	Acetylene	Ethylene	Ethane	Propylene
8.4 eV	$C_3H_8$	$O_2$	0.040	0.028	0.080	0.015	0.23
10 eV	$C_3H_8$	$O_2$	.115	.073	.22	.043	.17
11.6–11.8 eV	$C_3H_8$	$O_2$	.22	.22	.27	.0585	.13
16.7–16.8 eV	$C_3H_8$	$O_2$	.27	.001	.084	.46	.32
		NO	.29	.001	.072	.42	.36
	$C_3D_8$	$O_2$	.29	.001	.052	.43	.14
		NO	.27	.001	.060	.48	.23
21.2 eV	$C_3H_8$	$O_2$	.29	.018	.113	.37	.405
		NO	.27	.018	.13	.37	.40
	$C_3D_8$	$O_2$	.28	.023	.092	.41	.23
		NO	.31	.020	.095	.40	.24

Pressure = 3.0 torr.

explanation of the fact that the propylene yield drops off at high conversions is that propylene product may be removed by reaction with ions or H atoms in the system. It has been shown [15, 16] that H atoms add to propylene faster than to ethylene or acetylene. Apparently, at the relatively low pressures at which the experiments are carried out, oxygen is not a very effective interceptor of hydrogen atoms.

In table 2, the experiments were carried out under conditions where no more than  $3 \times 10^{15}$  quanta were absorbed by propane at a pressure of 3 torr in the reaction cell. Thus, the yields of propylene shown in table 2 have not been much affected by these secondary processes.

Table 2 shows the quantum yields of products formed in  $C_3H_8$  and  $C_3D_8$  irradiated with 8.4, 10.0, 11.6–11.8, 16.7–16.8, and 21.2 eV photons in the presence of 5 percent  $O_2$  or NO added as a radical scavenger. As the photon energy is increased the amount of energy to be distributed among the fragments will be larger and secondary decompositions will become more prevalent. For instance the formation of acetylene, whose quantum yield of production is seen to increase with energy from 8.4 to 11.6–11.8 eV, can be attributed to the decomposition of  $C_2H_4$  and  $C_3H_6$  formed in primary processes 2 and 3 respectively. It is of interest that at 16.7–16.8 eV, where only ionic processes lead to end product formation, the quantum yield of acetylene is negligible ( $\sim 0.001$ ). This observation is not unexpected because as shown by Cermak and Herman [20] none of the fragmentation processes of the  $C_4H_8^+$  ion formed by collision with metastable neon atoms yields  $C_2H_2$  as a neutral product. Furthermore, there are no known ion-molecule reactions involving fragments from  $C_3H_8^+$  which would ultimately result in the formation of  $C_2H_2$  [21–27].

Thus, the result that acetylene formation from ionic processes (i.e., in the 16.7–16.8 eV photolysis) in propane is negligible, confirms the assumption made earlier [18], that all acetylene formed in the radiolysis of propane has neutral excited propane molecules,

rather than ions, as precursor. The estimate that the ratio of neutral excited molecule formation to ionization is 0.4 in the radiolysis of propane [18], based on this assumption is, thus, probably approximately correct.

Considering that acetylene formation can apparently all be ascribed to a neutral excited propane precursor, it is interesting that the yield of acetylene increases ten-fold when the photon energy is raised from 16.7–16.8 eV to 21.2 eV (table 3). This is in agreement with the tentative conclusion reached above, that at 21.2 eV as many as 7 percent of the activated species may dissociate as neutral excited molecules before an electron can be ejected.

It is of interest to note that according to the quantum yield data given in table 2, the probability of the elimination of an alkane from neutral excited propane (processes (1) and (2)) increases with the energy of the photon [28]. The increase probably occurs at the expense of the  $H_2$  elimination process (3). In a recent study on the far ultraviolet photolysis of ethane [29] a similar trend was seen. In that case, however, all molecular elimination processes decrease at the expense of direct bond cleavage processes as the energy is increased further. Similar trends can be expected for propane. The data given in table 2 do not allow a more detailed analysis of the primary processes occurring in propane in the 8.4–11.8 eV energy range. Quantum yields of all free radicals have to be known as well. A partial analysis of the role of free radicals in the decomposition of neutral excited propane is given elsewhere [18, 19, 30, 31].

### 3.4. Isotopic Labeling Experiments

In table 3 are given the isotopic distributions of the major lower hydrocarbon products formed in the photolysis of a  $C_3H_8$ - $C_3D_8$  (1:1) mixture in the presence of a radical scavenger with 16.7–16.8 and 21.2 eV photons.

The product ethane is known [5, 27, 32] to be formed in the reactions of ethyl ions with propane:



and in the ethylene ion reaction:



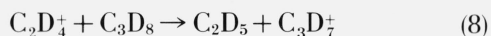
It can be estimated from the relative amounts of  $\text{C}_2\text{D}_5\text{H}$  and  $\text{C}_2\text{D}_4\text{H}_2$  formed in these experiments at 16.7–16.8 eV, that about 75 percent of the ethane resulted from the ethyl ion reaction, and about 25 percent from the ethylene ion reaction. On this basis, since the ethyl ion does not undergo any alternate reactions with propane [27] we can estimate roughly that the ion pair yield of the ethyl ion in the 16.7–16.8 eV photolysis of propane is about 0.32–0.34; the ion pair yield of this ion observed in the mass spectrometric study in which propane ions were generated by collision with metastable neon atoms [20] was 0.37. Using the same reasoning, it can be estimated that at 21.2 eV, 89 percent of the ethane originates from the reaction of an ethyl ion precursor. This gives an approximate ion pair yield for the ethyl ion in the photolysis at 21.2 eV of  $\sim 0.33$ ; when  $\text{C}_3\text{H}_8^+$  ions are generated in a mass spectrometer through collision with metastable helium atoms [20], the ion pair yield of ethyl ions observed was 0.25.

TABLE 3. *Photolysis of  $\text{C}_3\text{H}_8\text{-C}_3\text{D}_8$  (1:1); isotopic compositions of products*

Photon Energy	Ethanes			Methanes	Propylenes	Ethylenes
	$\text{C}_2\text{D}_6$	$\text{C}_2\text{D}_5\text{H}$	$\text{C}_2\text{D}_4\text{H}_2$	$\text{CD}_3\text{H}/\text{CD}_4$	$\text{C}_3\text{D}_5\text{H}/\text{C}_3\text{D}_6$	$\text{C}_2\text{D}_3\text{H}/\text{C}_2\text{D}_4$
16.7-16.8 eV	1.00	0.75	0.25	0.057	0.32	0.63
21.2 eV	1.00	.95	.12	.051	.33	.46

Pressure = 3 torr.  
5 percent  $\text{O}_2$  added.

The yields of ethanes formed in reactions such as 7 from ethylene ion precursors do not directly give us the yield of the ethylene ion, since this ion can also undergo an  $\text{H}^-$  (or  $\text{D}^-$ ) transfer reaction with propane:



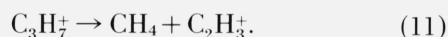
to form an ethyl radical, which in these experiments will be scavenged. However, in one experiment  $\text{H}_2\text{S}$  was added to  $\text{C}_3\text{D}_8$  irradiated with 21.2 eV photons. In this system, the deuterated ethyl radical formed in reaction 8 will react with  $\text{H}_2\text{S}$  to form  $\text{C}_2\text{D}_5\text{H}$ :



while all other ethane-forming reactions will give fully deuterated ethane,  $\text{C}_2\text{D}_6$ . From the observed yield of  $\text{C}_2\text{D}_5\text{H}$ , it could be deduced that for an ethylene ion reacting with propane- $\text{d}_8$ , the ratio of  $\text{D}^-/\text{D}_2^-$  transfer reactions is 0.9. This value is in reasonably good agreement with the results of Sieck and Searles [33], who recently ascribed a value of 0.8 to this ratio on the basis of results obtained in the NBS high pressure photoionization mass spectrometer. (They found that the ratio

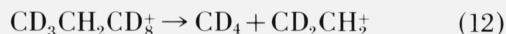
of  $\text{H}^-/\text{H}_2^-$  transfer reactions for ethylene ions reacting with  $\text{C}_3\text{H}_8$  was 1.15.) On this basis, we can estimate ion pair yields for the ethylene ion generated in the 16.7–16.8 eV photolysis or the 21.2 eV photolysis of propane of about 0.22 and 0.08, respectively. The corresponding ion pair yields of ethylene ions generated in a mass spectrometer by collision with metastable neon and helium atoms are 0.20 and 0.17.

Because the methane formed in the photolysis of  $\text{C}_3\text{H}_8\text{-C}_3\text{D}_8$  (1:1) mixture contains very little partially deuterated product, it must be formed almost exclusively in the unimolecular decompositions:



Process (11) and/or further decomposition of  $\text{C}_2\text{H}_4^+$  formed in process (10) must be of importance in view of the fact that the estimated quantum yields of  $\text{C}_2\text{H}_4^+$  are lower than the quantum yield of molecular methane (table 2).

From studies on  $\text{CD}_3\text{CH}_2\text{CD}_3$ , the fragmentation of the propane ion to form an ethylene ion (process 10) is known to occur through two mechanisms. The lower energy process (A.P. = 11.8 eV) [34] is a 1,3 elimination of methane from the propane ion:



and the higher energy process (A.P. = 12.2 eV) [34] is a 1,2 elimination:



It is of interest then that the observed ratio  $\text{CD}_3\text{H}/\text{CD}_4$  (table 4) indeed increases from 0.69 at 16.7–16.8 eV to 0.76 at 21.2 eV. In an earlier study [34], it was noted that  $\text{CD}_3\text{CH}_2\text{CD}_3^+$  ions generated by charge exchange with  $\text{Xe}^+$  ions (12.1–13.4 eV) underwent processes 12 and 13 to give a  $\text{CD}_3\text{H}/\text{CD}_4$  ratio of 0.35.

Because the ethylene and propylene contain large fractions of partially deuterated products (table 3), it is evident that an important mode of formation of these products is bimolecular ion-molecule reactions such as, for instance:

TABLE 4. *Photolysis of  $\text{CD}_3\text{CH}_2\text{CD}_3$ ; isotopic composition of methane*

Photon Energy	$\text{CD}_3\text{H}/\text{CD}_4$
16.7-16.8 eV	0.69
21.2 eV	.76

Pressure = 3 torr.  
5 percent  $\text{O}_2$  added.



Reaction 14 is thought to proceed through formation of a condensation ion,  $C_5D_3H_8^+$ , which will dissociate to form other partially deuterated ethylenes besides  $C_2D_3H$  [27]. Reaction 15 is a simple hydride transfer reaction.

For a more detailed discussion on the neutral end-product resulting from ion-molecule reactions we refer the reader to earlier studies [5, 18, 27, 32, 35].

#### 4. References

- [1] Gorden, R. Jr., Rebbert, R. E., and Ausloos, P., Nat. Bur. Stand. (U.S.), Tech. Note 496, 55 pages (Oct. 1969).
- [2] Back, R. A., and Walker, D. C., J. Chem. Phys. **37**, 2348 (1962).
- [3] Jensen, C. A., and Libby, W. J., J. Chem. Phys. **9**, 2831 (1968).
- [4] Rebbert, R. E., and Ausloos, P., J. Am. Chem. Soc. **90**, 7370 (1968).
- [5] Lias, S. G., Rebbert, R. E., and Ausloos, P., J. Chem. Phys. **52**, 773 (1970).
- [6] Fundamental Processes in Radiation Chemistry, P. Ausloos, Ed., (Interscience Publishers, New York, N. Y., 1968).
- [7] Ausloos, P., Rebbert, R. E., and Lias, S. G., J. Phys. Chem. **72**, 3904 (1968).
- [8] Rebbert, R. E., and Ausloos, P., J. Res. Nat. Bur. Stand. (U.S.), **75A** (Phys. and Chem.), No. 5, 481-486 (Sept.-Oct. 1971).
- [9] Bennett, S. W., Tellinghuisen, J. B., Phillips, L. F., J. Phys. Chem. **75**, 719 (1971).
- [10] Cook, G. R., and Metzger, P. H., J. Opt. Soc. Am. **54**, 968 (1964).
- [11] Cook, G. R., Metzger, P. H., Ogawa, M., Becker, R. A., and Ching, B. K., Aerospace Corp. Report No. TDR-469 (9260-01)-4 (1965).
- [12] Rebbert, R. E., and Ausloos, P., unpublished results.
- [13] Metzger, P. H., and Cook, G. R., J. Chem. Phys. **41**, 642 (1964).
- [14] Schoen, R. I., J. Chem. Phys. **37**, 2032 (1962).
- [15] Cowfer, J. A., Keil, D. K., Michael, J. V., and Yeh, C., J. Phys. Chem. **75**, 1584 (1971) and references cited therein.
- [16] Daby, E. E., Niki, H., and Weinstock, B., J. Phys. Chem. **75**, 1601 (1971) and references cited therein.
- [17] McNesby, J. R., and Okabe, H., Advan. Photochem. **3**, 157 (1964).
- [18] Ausloos, P., and Lias, S. G., J. Chem. Phys. **44**, 521 (1966).
- [19] Ausloos, P., and Lias, S. G., Ber. Bun. Physik. Chem. **72**, 187 (1968).
- [20] Cermak, V. and Herman, Z., Coll. Czechoslov. Chem. Commun. **30**, 169 (1965).
- [21] Ryan, K. R., and Futrell, J. H., J. Chem. Phys. **42**, 819 (1965).
- [22] Petterson, E., and Lindholm, E., Arkiv. Fysik **24**, 49 (1963).
- [23] Munson, M. S. B., Franklin, J. L., and Field, F. H., J. Phys. Chem. **68**, 3098 (1964).
- [24] Derwish, G. A. W., Galli, A., Giardini-Guidoni, A., and Volpi, G. G., J. Chem. Phys. **41**, 2998 (1964).
- [25] Aquilanti, V., and Volpi, G. G., J. Chem. Phys. **44**, 2307 (1966).
- [26] Sieck, L. W., and Futrell, J. H., J. Chem. Phys. **45**, 560 (1966).
- [27] Bone, L. I., and Futrell, J. H., J. Chem. Phys. **46**, 4084 (1967).
- [28] At 11.6-11.8 eV fragmentation of the  $C_3H_8^+$  ion may contribute to the formation of  $CH_4$ . However at the pressures used in this study, the unimolecular decomposition of  $C_3H_8^+$  is entirely quenched.
- [29] Lias, S. G., Collin, G. J., Rebbert, R. E., and Ausloos, P., J. Chem. Phys. **52**, 1841 (1970).
- [30] Vorachek, J. H., and Koob, R. D., J. Phys. Chem. **74**, 4455 (1970).
- [31] Dhirga, A. K., and Koob, R. D., J. Phys. Chem. **74**, 4490 (1971).
- [32] Ausloos, P., Lias, S. G., and Sandoval, I. B., Disc. Faraday Soc. **36**, 66 (1963).
- [33] Sieck, L. W., and Searles, S. K., J. Am. Chem. Soc. **92**, 2937 (1970).
- [34] Futrell, J. H., and Tiernan, T. O., J. Chem. Phys. **39**, 2539 (1963).
- [35] Bone, L. I., Sieck, L. W., and Futrell, J. H., The Chemistry of Ionization and Excitation, G. R. A. Johnson and G. Scholer, Eds., Taylor and Francis Ltd., London (1967).

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